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(54) IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF ALCOHOLS AND ESTERS

(71) We, CELANESE CORPORATION, of 522 Fifth Avenue, New York 36, State of New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of alcohols and carboxylic acid esters.

It is known that an ethylenically unsaturated compound can be hydrated to give an alcohol by reaction with water or converted into an ester by reaction with a carboxylic acid, and a large number of catalysts have been proposed for use in carrying out these reactions.

According to the present invention, the production of an alcohol, a carboxylic acid ester or a mixture thereof, comprises contacting an ethylenically unsaturated compound with a liquid medium comprising a carboxylic acid, a free heteropoly acid of molybdenum or tungsten and, if an alcohol is to be obtained, water.

It is to be noted that, in carrying out the process of the invention, a carboxylic acid is present even when the sole or main product desired is an alcohol. It seems possible that the ethylenically unsaturated compound first reacts with the carboxylic acid to form an ester which, in the presence of water, is hydrolysed to form an alcohol. Certainly somewhat higher temperatures seem best when producing an alcohol than are optimum for ester production and, moreover, alcohol production is favoured by the presence of a hydrolysis catalyst, e.g. phosphoric acid, benzene sulphonic acid or, especially, sulphuric acid. When it is desired to have a hydrolysis catalyst present it may form, for example, from 0.1 to 10 weight per cent of the total liquid present.

The carboxylic acid used in the process of the invention may be a monocarboxylic acid or may contain more than one carboxylic group and may be aromatic or non-aromatic, unsubstituted or substituted with, for instance, halo, hydroxyl, nitro, amino, sulpho, carbonyl, or alkoxy substituents. Specific examples of carboxylic acids which may be used are formic, acetic, propionic, valeric, terephthalic, tetrachloroterephthalic, chloroacetic, adipic, succinic, butyric, acrylic, isophthalic, methacrylic, monomethyl terephthalic, crotonic, caproic, n-undecyclic, sorbic, palmitic, stearic, oleic, cis-erucic, oxalic, azelaic, maleic, glycollic, malic, levulinic, abietic, benzoic, nitrobenzoic, phenylacetic, picolinic and furoic acids. The preferred carboxylic acids are those of 1 to 20 carbon atoms which are free from ethylenic and acetylenic unsaturation and are of the formula R—COOH wherein R is a hydrocarbon or carboxyl-substituted hydrocarbon radical, with the aliphatic carboxylic acids such, for instance, as formic acetic and succinic acids, being especially preferred. The amount of carboxylic acid present may, in general, amount to from 0.05 to 100, and preferably 0.8 to 10.0, equivalents per mole of ethylenically unsaturated compound.

The heteropoly acids used as catalysts in the process are well known compounds containing in the molecular a number of replaceable hydrogen ions as well as a complex and high molecular weight anion. These free acids are generally very water soluble and in crystalline form are almost always highly hydrated. The heteropolyanions of these free acids contain various numbers of molybdenum or tungsten ions around a central atom, sometimes referred to as the hetero-atom. In some instances a portion of the molybdenum or tungsten ions is replaced by pentavalent vanadium or niobium. The ratio of the number of tungsten or molybdenum atoms to the central atoms may vary widely but, in the compounds used in the process of the invention, is generally between 6:1 and 12:1, especially good results being obtained with

compounds in which the ratio is from 9:1 to 11:1. As many as 36 different elements have been reported to function as central ions. Preferably the catalyst used according to the invention contains central ions of phosphorus, manganese or arsenic; other elements which may form the central ions are silicon, germanium, titanium, cobalt, iron, aluminium, chromium, zirconium, gallium, tellurium and boron. The free heteropolymolybdic and heteropolytungstic acids are generally named so as to indicate both the ratio of molybdenum or tungsten to the central atom and the nature of the central atom. Thus

$$H_3(PMo_{12}O_{40}) . 59H_2O$$

is named 12-molybdophosphoric acid and

$$H_6(P_2Mo_{18}O_{62}) . 48H_2O$$

is named 10-molybdophosphoric acid, the latter compound being the preferred catalyst. Other free heteropolyacids of molybdenum or tungsten useful as catalysts in the process of the invention are dimeric 9-molybdophosphoric acid,

$$H_6(P_2Mo_{18}O_{62}) . xH_2O;$$

dimeric 9-tungstophosphoric acid,

$$H_6(P_2W_{18}O_{62}) . xH_2O;$$

12-tungstotelluric acid,

$$H_6(TeW_{12}O_{42}) . 25H_2O;$$

11-tungstoaluminic acid,

$$H_{10}(Al_2W_{22}O_{74}) . 44H_2O;$$

vanadotungstoselenic acid,

$$H_2SeO_4 . 10WO_3 . V_2O_5 . xH_2O;$$

dimeric 9-molybdoarcenic acid,

$$H_6(As_2MO_{18}O_{62}) . xH_2O;$$

9-molybdomanganic acid,

$$H_6(MnMo_9O_{32}) . xH_2O;$$

12-tungstosilicic acid,

$$H_4(SiW_{12}O_{40}) . xH_2O;$$

and 12-molybdosilicic acid,

$$H_4(SiMo_{12}O_{40}) . xH_2O.$$

The ethylenically unsaturated compounds which may be converted in the process of the invention are, in general, those compounds which have at least one ethylenic double bond present with ethylenically unsaturated hydrocarbons being the usual starting material. Best results are obtained when converting ethylenically unsaturated hydrocarbons of 2 to 30 carbon atoms which are free of acetylenic unsaturation, especially those non-aromatic hydrocarbons of 3 to 15 carbon atoms which have a single ethylenic double bond as the only unsaturation and which have at least one hydrogen atom connected to a carbon atom adjacent the ethylenic unsaturation, e.g. the alpha-olefines such as isobutylene. Some specific ethylenically unsaturated compounds which may be used in the process of the invention are propylene, butene-1, octene-2, cyclohexene, butadiene, hexene-2, 2-methylbutene-1, cyclooctadiene, styrene, indene, stilbene, 1-vinyl-1-propene, vinyl cyclohexane, decene-2, propylene tetramer, pinene, isobutylene, decene-1, butene-2, allyl alcohol and allyl chloride. In most cases it has been found that the products formed in the present process are those products expected from Markownikoff's Rule. Thus isopropyl alcohol and/or an isopropyl ester such as isopropyl acetate may be formed from propylene and octane-2-ol and/or a 2-hydroxy octyl carboxylate from octene-1. Ethylene is one notable exception as it is usually converted to butane-2-ol or the corresponding ester.

The operating conditions used may vary widely but the temperature should generally be between 0 and 200°C. The pressure should be enough to maintain a liquid phase in the reaction zone and may vary from subatmospheric pressures to 500 psig. When operating under essentially anhydrous conditions so that an ester is the main product, the temperature is preferably between 20 and 140°C. while the pressure is up to 3000 psig. Usually slightly more severe conditions are required when operating in the presence of water so as to produce an alcohol than when operating under anhydrous conditions, the preferred temperature conditions, when operating with substantial amounts of water present, being from 50 to 175°C. with the pressures up to 4000 psig.

Since the heteropolyanions of the catalysts used are generally decomposed by strongly basic solutions, the process should generally be carried out under conditions such that the pH remains below 9.0 and preferably below 7.0. The amount of the heteropolyacid used is generally between 10^{-6} and 10^{-1} moles, preferably 10^{-4} to 10^{-2} moles, of the free heteropolyacid per mole of the ethylenically unsaturated compound being converted.

The process may be carried out continuously, intermittently or batchwise and the reactants may be introduced into the reaction zone in any order. Stirring the reactants or the use of other forms of agitation is not necessary but reduces the time required to

complete the reaction by promoting intimate contact of the reactants. Inert solvents may be present, if desired, but are not generally necessary.

The following Examples illustrate the invention: —

EXAMPLE 1

A stirred one-litre Parr bomb was charged with 100 millilitres of water, 118 grams of succinic acid and 2 grams of 10-molybdophosphoric acid and then the bomb and its contents were cooled to −75°C. by immersion in a dry ice-acetone bath. 84 grams of propylene which had been liquefied by cooling it in a dry ice-acetone bath were then added to the Parr bomb and the bomb sealed, heated to 160°C. for 120 minutes and then rapidly cooled to ambient temperature by immersion in an ice water bath. The propylene remaining was slowly bled off and the remaining contents of the bomb analysed by gas chromatography. Analysis showed that approximately 10% of the propylene charged had been converted to isopropyl alcohol.

EXAMPLE 2

The procedure of Example 1 was repeated except that the charge consisted of 100 millilitres of water, 50 grams of succinic acid, 2 grams of 10-molybdophosphoric acid, 84 grams of propylene and 5 millilitres of sulphuric acid and the temperature used was 140°C. Analysis of the product showed that approximately 40% of the propylene charged had been converted to isopropyl alcohol.

EXAMPLE 3

The procedure of Example 1 was repeated except that the charge consisted of 100 millilitres of butyric acid, 70 grams of propylene and 1 gram of 10 molybdophosphoric acid, the temperature used was 120°C. and the reaction time one hour. Analysis of the reaction product showed that 90% of the propylene had been converted to isopropyl butyrate.

EXAMPLE 4

The procedure of Example 1 was repeated except that the charge consisted of 200 millilitres of acetic acid, 70 grams of propylene and 2 grams of 12-tungstophosphoric acid and the temperature used was 120°C. Analysis of the reaction product showed that 5% of the propylene had been converted to isopropyl acetate.

EXAMPLE 5

The procedure of Example 1 was repeated except that the charge consisted of 200 grams of acetic acid, 72 grams of propylene and 0.54 grams of 10-molybdophosphoric acid, the temperature used was 125°C. and the reaction time one hour. Analysis of the reaction product showed that 88.8% of the propylene had been converted to isopropyl acetate.

EXAMPLE 6

The procedure of Example 1 was repeated except that the charge consisted of 156 grams of acetic acid, 49 grams of water, 80 grams of propylene and 0.57 grams of 10-molybdophosphoric acid and the reaction time was three hours. Analysis of the reaction product showed that 65% of the propylene had been converted and, of the propylene converted, 66.9% went to isopropyl acetate and 33.1% to isopropyl alcohol.

EXAMPLE 7

The procedure of Example 1 was repeated except that the charge consisted of 240 grams of formic acid, 110 grams of propylene and 3.5 grams of 10-molybdophosphoric acid, the temperature used was 100°C. and the reaction time 18 minutes. Analysis of the reaction product showed that 85% of the propylene charged had been converted to isopropyl formate.

EXAMPLE 8

The procedure of Example 1 was repeated except that the charge consisted of 175 grams of formic acid, 23 grams of water, 97 grams of propylene and 3 grams of 10-molybdophosphoric acid and the temperature used was 165°C. Analysis of the reaction product showed that 82.6% of the propylene charged had been converted with 94.2% of the propylene converted going to isopropyl formate and 5.8% to isopropyl alcohol.

EXAMPLE 9

The procedure of Example 1 was repeated except that the charge consisted of 23 grams of formic acid, 180 grams of water, 72 grams of propylene and 2.8 grams of 10-molybdophosphoric acid and the temperature used was 210°C. Analysis of the reaction product showed that 26.5% of the propylene charged had been converted with 6.8% of the propylene converted going to isopropyl formate and 93.2% to isopropyl alcohol.

EXAMPLE 10

25 millilitres of cyclohexene, 25 millilitres of acetic acid and 0.5 grams of 10-molybdophosphoric acid were put in a pressure bottle at room temperature and the bottle sealed. The pressure bottle was then immersed in a constant temperature bath at 100°C. for one hour and then cooled to room temperature. Gas chromatography analysis of the contents of the pressure bottle showed that 34% of the cyclohexene charged had been converted to cyclohexyl acetate.

EXAMPLE 11

Example 10 was repeated using 9-molybdo-

phosphoric acid instead of 10-molybdophosphoric acid and practically identical results were obtained.

EXAMPLE 12

50 millilitres of acetic acid containing 0.25 grams of 10-molybdophosphoric acid were put in a flask and then isobutylene was bubbled into the flask at room temperature, approximately 25°C. After one hour the temperature in the flask had risen to 35°C. and the liquid in the flask contained 48 weight per cent of t-butyl acetate. Of the isobutylene converted, more than 85% had been converted to t-butylacetate.

EXAMPLE 13

A three-neck, 12-litre flask, fitted with a reflux condenser and a mechanical stirrer, was charged with 35 grams of 10-molybdophosphoric acid, 1400 grams of decene-1 and 4200 grams of acetic acid. The mixture was refluxed for 16 hours and upon distillation the following four cuts were made:— (1) 75 grams of a mixture of acetic acid, water and decene-1, (2) 450 grams of unreacted decene-1, (3) 60 grams of a mixture of decene and decyl acetate, and (4) 900 grams of 3-decyl acetate of more than 98% purity.

WHAT WE CLAIM IS:—

1. Process for the production of an alcohol, a carboxylic acid ester or a mixture thereof, which comprises contacting an ethylenically unsaturated compound with a liquid medium comprising a carboxylic acid, a free heteropoly acid of molybdenum or tungsten and, if an alcohol is to be obtained, water.

2. Process according to Claim 1, wherein said liquid medium is anhydrous and is maintained at a temperature of from 20 to 140°C.

3. Process according to Claim 1, wherein said liquid medium contains water and also a hydrolysis catalyst and is maintained at a temperature of from 50 to 175°C.

4. Process according to Claim 1, 2 or 3, wherein the ethylenically unsaturated compound employed is a hydrocarbon containing a single ethylenic bond as the only unsaturation.

5. Process according to Claim 4, wherein the ethylenically unsaturated compound employed is propylene.

6. Process according to any of the preceding claims, wherein the carboxylic acid used is formic acid or acetic acid.

7. Process according to any of the preceding claims, wherein the heteropoly acid used is a heteropolymolybdic acid having a central atom of phosphorus, manganese or arsenic, and in which the ratio of molybdenum atoms to central atoms is from 9:1 to 11:1.

8. Process according to Claim 7, wherein the heteropolyacid used is 10-molybdophosphoric acid.

9. Process for the production of an alcohol, a caraboxylic acid ester or a mixture thereof according to Claim 1, substantially as hereinbefore described.

10. Process for the production from propylene of isopropyl alcohol or an ester thereof, substantially as described in any of Examples 1 to 9.

11. Alcohols and carboxylic acid esters, whenever produced by any of the processes claimed in the preceding claims.

A. J. BUTTERWORTH,
Chartered Patent Agent,
Brettenham House,
Lancaster Place, Strand,
London, W.C.2.

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